Novel Nitronyl Nitroxides: Synthesis and Properties

Stefan Greve[a], Volkmar Vill[b], and Willy Friedrichsen[a]

[a] Institute of Organic Chemistry, University of Kiel, Otto-Hahn-Platz 3,
D-24118 Kiel, Germany
[b] Institute of Organic Chemistry and Biochemistry, University of Hamburg,
Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

Reprint requests to Prof. Dr. W. Friedrichsen. E-mail: friedrichsen@oc.uni-kiel.de

Z. Naturforsch. **57b,** 677–684 (2002); received February 21, 2002

Nitronyl Nitroxides, Mesogenic Behaviour

The synthesis of several new nitronyl nitroxides with mesogenic groups is reported (**6a, b**, **11**, **14a, b**). Microscopic investigations revealed that in some cases (**6b**, **14b**) highly ordered mesogenic phases are formed.

Introduction

Liquid crystalline radicals with a neutral π-delocalized spin system seem to be unknown [1, 2]. Among organic radicals, nitronyl nitroxides (NIT) because of their stability are of considerable interest in this respect. Compounds of this type [3, 4] have been used extensively as building block(s) for magnetic materials [5]. Ferromagnetism in compounds with an NIT moiety [6, 7] suggests the possibility of ferromagnetic liquid crystals with this structure element [8]. Therefore preliminary investigations have been carried out to find out whether mesogenic phases of this type are accessible [9].

Preparative Results

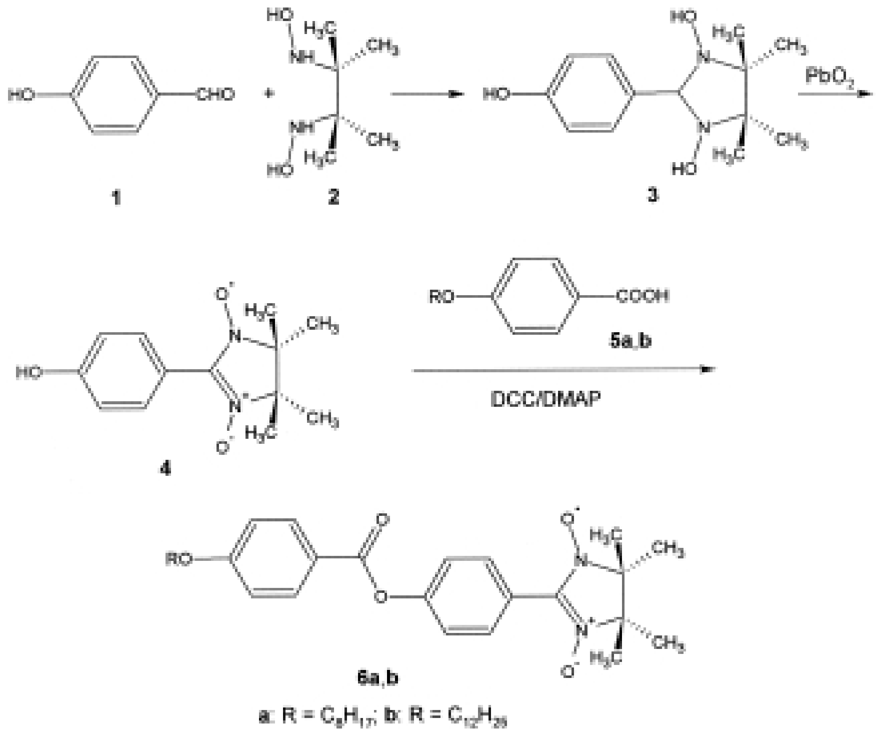
A rod-like geometry [11] seems to be a good prerequisite for a liquid crystalline NIT compound. Therefore compound **4** (Scheme 1) was chosen as starting material.

As has been reported as early as 1968 [3,12] this compound is readily available from 4-hydroxybenzaldehyde (**1**) and bishydroxylamine **2** *via* **3**, although the yield in the dehydrogenation step was quite low (19%) [12]. This could be improved to 26%. Treatment of **4** with 4-octyloxy- and 4-(dodecyloxy)benzoic acid (**5a, b**) under Steglich conditions [13] (DCC, DMAP) resulted in the formation of **6a** (62%) and **6b** (50%) as dark-blue crystals with mp. 85 °C and 90 °C, respectively.

The syntheses of **11** and **14a, b** are also straightforward. Etherification of aldehyde **1** with alkylbromide **7b** yields **8** which after treatment with **2** gives 1,3-dihydroxyimidazolidine derivative **9** as colorless crystals, which is already oxidized by air. Treatment with lead dioxide gives the cyclic nitronyl nitroxide**10** in 81% yield as dark blue needles. Esterification with **5b** under Steglich conditions gives **11** in 63% yield as blue crystals. The synthesis of **14a, b** can be accomplished with **12a, b** as starting materials. Esterification with **1** (to form **13a, b**) and Jones oxidation [14] yields carboxylic acids **13c, d**. Treatment of these acids with **10** under Steglich conditions gives nitroxides **14a** and **14b** as blue crystals with m.p. 64 °C and 91.5 °C, respectively.

In order to get an insight into the liquid crystal (LC) behavior of **6a, b**, **11**, and **14a, b** microscopic measurements with a polarizing microscope were undertaken. Whereas compounds **6a**, **11**, and **14a** show no LC behavior, compound **6b** has a monotropic mesophase. Similar observations were made for compound **14b**. The crystals of compound **6b** melt at 90 °C to an isotropic liquid. On cooling, a mesophase is observed at 36 °C. At first glance, this mesophase looks like a typical nematic mesophase with Schlieren textures. The transition temperature is reproducible on cooling and heating again. The viscosity is high, similar to an ordered smectic or columnar phase. Very slow cooling from 36.5 °C to 35 °C yields a different texture with lancets typical for ordered smectic phases. The mesophase is not miscible with the nematic phase of PCH7 (4-(*trans*-4-heptylcyclohexylbenzonitrile)) [15a]. By annealing the melt around 40 °C, another crystalline form is obtained melting at 50 °C. The crystals of **14b** melt at 91.5 °C to an

0932–0776/2002/0600–0677 $06.00



Scheme 1.

isotropic liquid. On cooling, a mesophase is formed at 39 °C. This mesophase shows Schlieren and fan-shape textures similar to a smectic C phase. Slow cooling creates more homeotropic like textures. Faster cooling allows to supercool the melt down to 26 °C. Contact preparation with HOPDOB (4-hexyloxyphenyl 4-decyloxybenzoate) [15b] shows no miscibility of the mesophases. A second crystalline form melting at 49.5 °C is formed by annealing the supercooled melt below 45 °C. In both cases, the mesophases are most probably not low ordered phases (N, SC), but higher ordered phases. The viscosity of the mesophases are high, the textures obtained by slow cooling are not of an N or SC type and the phases are not miscible with phases of reference compounds.

Computational Results

Quantum chemical calculations of nitronyl nitroxides have been reported repeatedly [16a–d]. Semiempirical PM3 calculations [17a–c] of **15a** and **15b** show that geometry optimizations on this level of theory (see Table 1) agree reasonably well with experimental values (taken from [23]) with only one exception: the exocyclic N–O bond length was obtained as 1.24 Å, whereas experimental values are observed in the 1.28 Å region. Density functional theoretical calculations [18a–g, 19] reveal [20] that the B3LYP/6-31G* methodology gives geometrical data which are close to ex-

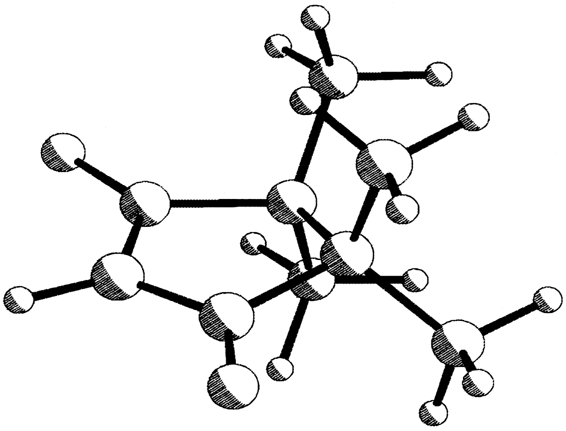
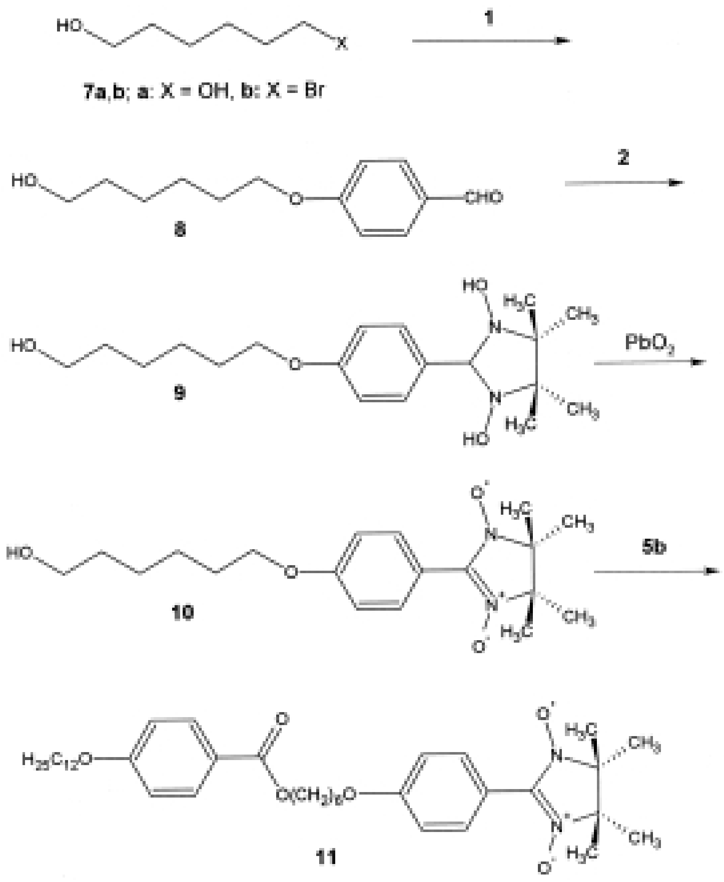
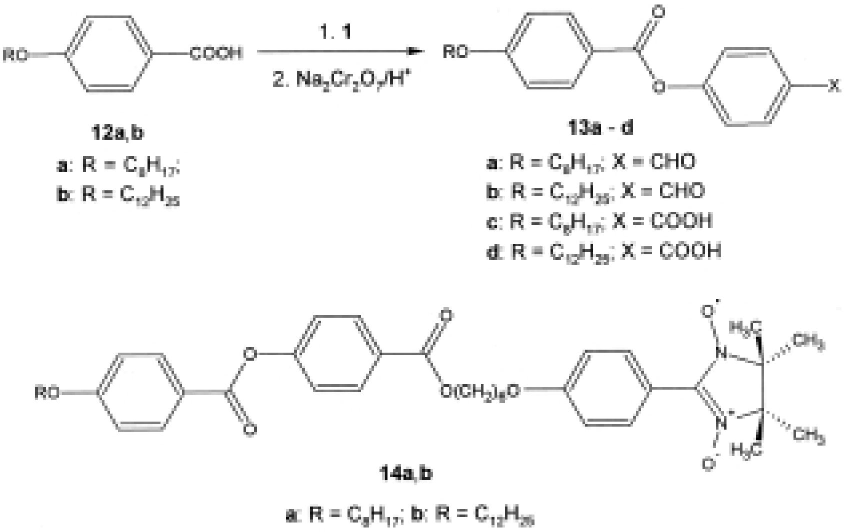


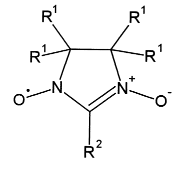
Fig. 1. Calculated structure of **15b** (B3LYP/6-31G*).



Scheme 2.



Scheme 3.



15a - d

a: $R^1 = R^2 = H$
b: $R^1 = Me$, $R^2 = H$
c: $R^1 = H$, $R^2 = Ph$
d: $R^1 = Me$, $R^2 = Ph$

Scheme 4.

perimental values (Table 1). Puckering of the five-membered ring in **15b** is also predicted correctly (Fig. 1) in contrast to PM3 results.

X-ray crystal structure determinations of 2-aryl-substituted nitronyl nitroxides have shown that in general there is a twist angle $\theta > 0°$ between the two rings [22]. PM3 calculations of **15d** show that the conformation with $\theta = 0°$ is an energy maximum. $\Delta H°_f$ decreases with increasing values of θ with its minimum at 90°. For **15c** similar results are obtained. However, DFT calculations (B3LYP/6-31G*) reveal the energy minimum at $\theta = 0°$, as is shown in Fig. 2.

The basis set dependence of the rotational barrier at this level of theory is negligible (B3LYP/6-31G*: 6.80 kcal/mol; 6-31G**: 6.97 kcal/mol). In conclusion it can be stated that although B3LYP/6-31G* calculations are in good agreement with experimental bond lengths (bond angles), PM3 data are sufficient for a preliminary inspection of molecules which are not conveniently treated computationally by *ab initio* and DFT methods.

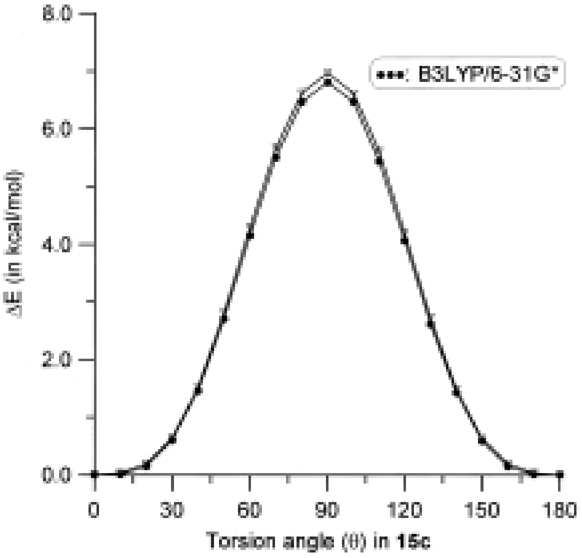


Fig. 2. Calculated rotational barrier around the C–Ph bond in **15c** (B3LYP/6-31G*, B3LYP/6-31G**).

The arrangement of the molecules of type **6** (**11**, **14**) in a highly ordered phase is unknown. Whereas the application of quantum chemical methods (*ab initio*, DFT) on large clusters of these molecules is beyond reach of comtemporary computer methodology, molecular mechanics methods may give an insight into preferred orderings. Starting with a rectangular arrangement of about 100 molecules of compound **6b** ($(C_{32}H_{45}N_2O_5)_{100}$ = $C_{3200}H_{4500}N_{200}O_{500}$) in *parallel* and *antiparallel* fashion optimizations using the force field MM+ were undertaken [24]. As can be seen from Fig. 3 the *parallel* arrangement is highly distorted whereas the *antiparallel* ordering (Fig. 4) is maintained during the optimization procedure. The same holds for molecules of type **14b** ($(C_{45}H_{61}N_2O_8)_{64}$ = $C_{2880}H_{3904}N_{128}O_{512}$; Fig. 5). Therefore it is highly probable that in line with

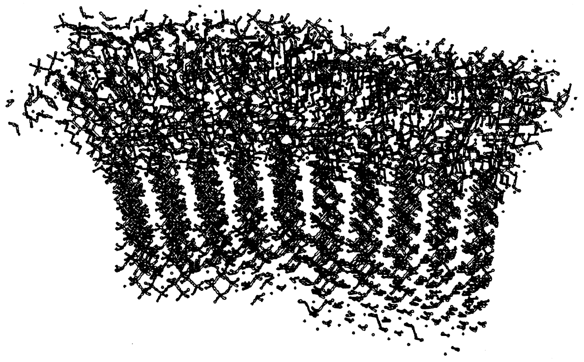


Fig. 3. Parallel ordering of molecules of **6b** (MM+ calculations).

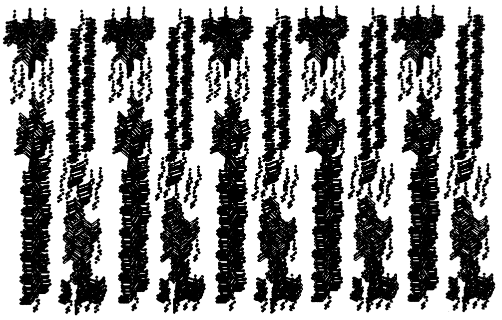


Fig. 4. Antiparallel ordering of molecules of **6b** (MM+ calculations).

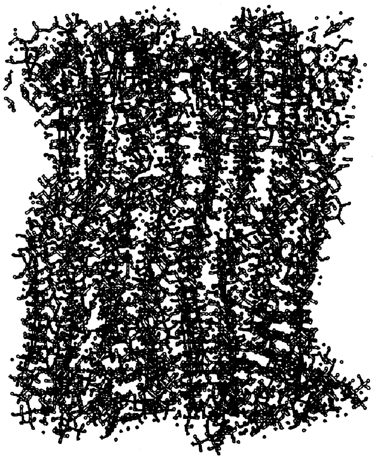


Fig. 5. Antiparallel ordering of molecules of **14b** (MM+ calculations).

expectations in an ordered phase molecules of this type are arranged predominantly or exclusively in an antiparallel fashion.

Experimental Section

All melting points were determined on a Dr Tottoli melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FTIR 1600 spectrophotometer. NMR spectra: Bruker AM 300 (300 MHz: FT ^{1}H NMR; 75 MHz: ^{13}C NMR); Bruker DRX 500 (500 MHz: FT ^{1}H NMR; 125 MHz: ^{13}C NMR); Varian EM 360 (60 MHz, ^{1}H NMR), internally referenced on Me_4Si ($CDCl_3$) or DMSO ([$^2H_6$]DMSO). *J* values are given in Hz. UV spectra: Zeiss DMR 10 spectrophotometer; mass spectra: Finnigan MAT 8230 and MAT 8200 mass spectrometer at 70 eV ionisation potential (EI) or by chemical ionisation (CI) (isobutane). Radial chromatography (RC) was carried out with a Harrison-Research Chromatotron on silica gel PF_{254} (Merck, Darmstadt). If assignments of spectral data are ambiguous, this is marked with asterisks (*,**).

Microscopic (texture) investigations were carried out with a polarizing microscope Olympus BH2 using a programmable heating device (Instec, Inc.).

Materials

All solvents were dried or purified using standard procedures [25]. 1,3-Dihydroxy-2-(4-hydroxyphenyl)-4,4,5,5-tetramethylimidazolidine (**3**) [12].

2-(4-Hydroxyphenyl)-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-3-imidazolio-1-oxyl (**4**)

A solution of 276 mg (1.1 mmol) **3** in benzene (50 ml) was treated with 1.40 g (5.9 mmol) of lead dioxide. The suspension was stirred vigorously, filtered after standing for further 2 h, evaporated, and the residue was purified by RC on silica gel with cyclohexane–ethyl acetate (1:1) to provide 71 mg (26%) of **4** as deep blue crystals with m.p. 144–146 °C (lit. [12] 134–135 °C).

2-{4-[(4-Octylbenzoyl)oxy]phenyl}-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-3-imidazolio-1-oxyl (**6a**)

To a solution of **4** (26.5 mg, 0.11 mmol), 4-octyloxybenzoic acid **5a** (27 mg, 0.11 mmol) and DMAP (5 mg) in dichloromethane (20 ml) was added 31 mg (0.15 mmol) of dicyclohexylcarbodiimide (DCC). After standing for 24 h, further 24 mg (0.12 mmol) of DCC was added, and the mixture was stirred for further 24 h. The solution was filtered, evaporated and the residue was purified by RC on silica gel with cyclohexane–ethyl acetate (1:1) to provide 32 mg (62%) **6a** as deep blue crystals with m.p. 85 °C. – IR (KBr): ν = 2920, 2852, 1720, 1392, 1364, 1256, 1166, 1071 cm^{-1}. – UV/vis (CH_3CN): λ_{max} (lg ε) = 213 (4.164), 274 (4.293), 350 (sh, 3.668), 615 (2.399) nm. – MS (EI, 70 eV): *m/z* (%) = 481 (29) [M$^+$]. – HRMS: $C_{28}H_{37}N_2O_5$: calcd. 481.2702; found 481.2702 (MS).

2-(4-{[4-(Dodecyloxy)benzoyl]oxy}phenyl)-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-3-imidazolio-1-oxyl (**6b**)

As described for the preparation of **6a**, from **4** (24.1 mg, 0.10 mmol), 4-dodecyloxybenzoic acid **5b (**30.6 mg, 0.10 mmol), DMAP (5 mg) and DCC (31 mg, 0.15 mmol) in dichloromethane (20 ml) 26.9 mg (50%) of **6b** was obtained as deep blue crystals with m.p. 90 °C. – IR (KBr): ν = 2922, 2851, 1733, 1390, 1365, 1257, 1159, 1050 cm^{-1}. – UV/vis (CH_3CN): λ_{max} (lg ε) = 212 (sh, 4.741), 274 (4.679), 349 (4.023), 364 (4.264), 587 (2.707) nm. – MS (EI, 70 eV): *m/z* (%) = 537 (14) [M$^+$]. – HRMS: $C_{32}H_{45}N_2O_5$: calcd. 537.3328; found 537.3326 (MS).

1,3-Dihydroxy-2-(6-hydroxyhexyloxy)phenyl-4,4,5,5-tetramethylimidazolidine (**9**)

A solution of **2** (222 mg, 1.5 mmol) and 4-(6-hydroxyhexyloxy)benzaldehyde **8** (0.333 g, 1.5 mmol) in 2-propanol (5 ml) was stirred for 12 h at 60 °C. After standing for further 12 h at 4 °C crystals of **8** were separated by filtration. Yield: 0.167 g

(32%) colorless crystals with m.p. 127–130 °C. – IR (KBr): ν = 3447, 2935, 1378, 1245 cm^{-1}. - ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.03 (s, 6H, CH$_3$), 1.06 (s, 6H, CH$_3$), 1.30–1.50 (m, 6H, CH$_2$), 1.70 (m, 2H, CH$_2$), 3.39 (m, 2H, CH$_2$), 3.94 (t, 2H, OCH$_2$), 4.37 (t, 1H, OH), 4.44 (s, 1H, CH), 6.86 (m, 2H, ar-H), 7.35 (m, 2H, ar-H), 7.68 (s, 2H, OH). – ^{13}C-NMR (75 MHz, [D$_6$]DMSO): δ = 17.19 (q), 24.44 (q), 25.33 (t), 25.47 (t), 28.81 (t), 32.52 (t), 60.67 (t), 65.92 (s), 67.38 (t), 89.95 (d), 113.55 (d), 129.59 (d), 133.89 (s), 158.11 (s).

2-[4-(6-Hydroxyhexyloxy)phenyl]-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-3-imidazolio-1-oxyl (**10**)

A solution of **9** (203 mg, 0.57 mmol) in ethanol (40 ml) was treated with lead dioxide (500 mg). After a few seconds the suspension showed a deep blue color. After stirring for 30 min the solution was filtered, evaporated and purified by RC on silica gel with cyclohexane–ethyl acetate (1:1). Yield: 0.163 g (81%) dark blue needles with m.p. 134 °C. – IR (KBr): ν = 3250, 2940, 2864, 1386, 1360, 1258, 1186 cm^{-1}. – UV/vis (CH$_3$CN): $\lambda_{\max}$ (lg ε) = 236 (3.820), 283 (4.221), 295 (sh, 4.110), 347 (sh, 3.764), 365 (3.985), 621 (2.715) nm. – MS (EI, 70 eV): *m/z* (%) = 349 (29) [M$^+$]. – HRMS: C$_{19}$H$_{29}$N$_2$O$_4$: calcd. 349.2127; found 349.2125.

2-{4-[(6-{[4-(Dodecyloxy)benzoyl]oxy}hexyl)-oxy]phenyl}-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-3-imidazolio-1-oxyl (**11**)

As described for **6a**, from **10** (28.0 mg, 0.08 mmol), 4-dodecyloxybenzoic acid (24.0 mg, 0.08 mmol), DMAP (5 mg) and DCC (27 mg, 0.13 mmol) 32 mg (63%) of **11** was obtained as dark blue crystals with m.p. 76–77 °C. – IR (KBr): ν = 2922, 2852, 1718, 1387, 1362, 1250, 1166, 1097 cm^{-1}. – UV/vis (CH$_3$CN): $\lambda_{\max}$ (lg ε) = 257 (4.570), 282 (4.361), 296 (sh, 4.200), 348 (3.896), 365 (4.081), 614 (2.894) nm. – MS (EI, 70 eV): *m/z* (%) = 637 (36) [M$^+$]. – HRMS: C$_{38}$H$_{57}$N$_2$O$_6$: calcd. 637.4217; found 637.4216.

4-Formylphenyl 4-(octyloxy)benzoate (**13a**)

Compound **12a** (5.00 g, 20.0 mmol) was esterified with **1** (2.44 g, 20.0 mmol) using the Steglich procedure [DMAP (184 mg, 1.51 mmol), DCC (4.50 g, 22.0 mmol), dichloromethane (35 ml), 24 h at r.t.]. Yield: 4.37 g (62%) colorless crystals of **13a** with m.p. 57 °C (lit. [26] 59 °C, clearing point 69 °C, lit. [26] 68 °C, *n*-hexane). – IR (KBr): ν = 2909, 2846, 1734, 1700, 1267, 1169 cm^{-1}. – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.90 (t, 3H, CH$_3$), 1.25–1.42 (m, 8H, CH$_2$), 1.43–1.55 (m, 2H, CH$_2$), 1.82 (m, 2H, CH$_2$), 4.05 (t, 2H, OCH$_2$), 6.98 (m, 2H, ar-H), 7.40 (m, 2H, ar-H), 7.97 (m, 2H, ar-H), 8.14 (m, 2H, ar-H), 10.03 (s, 1H, CHO). – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.10 (q), 22.65 (t), 25.98 (t), 29.08 (t), 29.22 (t), 29.32 (t), 31.80 (t), 68.40 (t), 114.45 (d), 120.82 (s), 122.60 (d), 131.21 (d), 132.43 (d), 133.90 (s), 155.93 (s), 163.89 (s), 164.21 (s), 190.94 (d).

4-Formylphenyl 4-(dodecyloxy)benzoate (**13b**)

Compound **12b** (2.50 g, 8.20 mmol) was esterified with **1** (1.20 g, 10.0 mmol) using the Steglich procedure [DMAP (92 mg, 0.75 mmol), DCC (2.25 g, 10.9 mmol), dichloromethane (20 ml), 24 h at r.t.]. Yield: 1.84 g (55%) fine, colorless crystals of **13b** with m.p. 64 °C (*n*-hexane). – IR (KBr): ν = 2912, 2848, 1736, 1699, 1268, 1169 cm^{-1}. – ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.88 (t, 3H, CH$_3$), 1.25–1.40 (m, 16H, CH$_2$), 1.40–1.55 (m, 2H, CH$_2$), 1.82 (m, 2H, CH$_2$), 4.05 (t, 2H, OCH$_2$), 6.98 (m, 2H, ar-H), 7.40 (m, 2H, ar-H), 7.97 (m, 2H, ar-H), 8.14 (m, 2H, ar-H), 10.03 (s, 1H, CHO). – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.14 (q), 22.99 (t), 25.97 (t), 29.07 (t), 29.36 (t), 29.56 (t), 29.60 (t), 29.64 (t), 29.66 (t), 31.92 (t), 68.39 (t), 114.42 (d), 120.42 (s), 122.61 (d), 131.23 (d), 132.43 (d), 133.87 (s), 155.91 (s), 163.88 (s), 164.23 (s), 191.01 (d).

4-{[4-(Octyloxy)benzoyl]oxy}benzoic acid (**13c**)

To a solution of **13a** (1.50 g, 4.2 mmol) in acetone (40 ml) Jones reagent (4 ml, prepared according to [27]) was added. The mixture was stirred for 2 h at r.t., added to crushed ice (200 g), stirred for further 30 min, the crystals were separated by filtration, washed with water and recrystallized from ethanol (50 ml). Yield: 1.31 g (84%) colorless crystals with m.p. 135 °C (lit. [26] 139 °C); clearing point 222 °C (lit. [26] 221 °C). – IR (KBr): ν = 3437, 2922, 1734, 1686, 1254, 1158 cm^{-1}. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.85 (t, 3H, CH$_3$), 1.20–1.34 (m, 8H, CH$_2$), 1.35–1.45 (m, 2H, CH$_2$), 1.73 (m, 2H, CH$_2$), 4.07 (t, 2H, OCH$_2$), 7.11 (m, 2H, ar-H), 7.39 (m, 2H, ar-H), 8.03 (m, 2H, ar-H), 8.07 (m, 2H, ar-H), 13.05 (s, br, 1H, OH). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 13.99 (q), 22.16 (t), 25.50 (t), 28.56 (t), 28.75 (t), 28.82 (t), 31.32 (t), 68.04 (t), 114.69 (d), 120.43 (s), 122.20 (d), 128.38 (s), 130.93 (d), 132.15 (d), 154.23 (s), 163.40 (s), 163.83 (s), 166.70 (d).

4-{[4-(Dodecyloxy)benzoyl]oxy}benzoic acid (**13d**)

Compound **13d** was prepared as described for **13c** from **13b** (7.00 g, 17.1 mmol) and Jones reagent (11.9 ml, prepared according to [27]) in acetone (120 ml). Yield: 4.3 g (61%) colorless needles, m.p. 111–113 °C (clearing point: 206 °C, from ethanol). – IR (KBr): ν = 2918, 2851, 1740, 1690, 1256, 1159 cm^{-1}. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.88 (t, 3H, CH$_3$), 1.19–1.42 (m, 18H, CH$_2$), 1.42–1.52 (m, 2H, CH$_2$), 4.04 (t, 2H, OCH$_2$), 6.98 (m, 2H, ar-H), 7.33 (m, 2H, ar-H), 8.12–8.22 (m, 4H, ar-H). – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 14.14 (q), 22.70 (t), 25.98 (t), 29.08 (t), 29.36 (t), 29.56 (t), 29.59 (t), 29.64 (t), 29.67 (t), 31.93 (t), 68.39 (t), 114.41 (d), 120.92 (s), 122.02 (d), 126.60 (s), 131.89 (d), 132.44 (d), 155.52 (s), 163.82 (s), 164.34 (s), 170.78 (s).

2-[4-({6-[(4-{[4-(Octyloxy)benzoyl]oxy}benzoyl)-oxy]hexyl}oxy)phenyl]-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-3-imidazolio-1-oxyl (**14a**)

Compound **13c** (31 mg, 0.09 mmol) was esterified with **10** (33 mg, 0.09 mmol) according to the Steglich procedure [DMAP (5 mg), DCC (19 mg) in dichloromethane (20 ml), 24 h at r.t., further DCC (19 mg) was added, 24 h at r.t.)]. The product was purified by RC on silica gel with cyclohexane–ethyl acetate. Yield 13.7 mg [22%; 24 mg (70%) of **13c** was recovered] blue crystals, m.p. 64 °C. – IR (KBr, CH$_2$Cl$_2$): ν = 2929, 1735, 1390, 1362, 1257, 1161 cm^{-1}. – UV/vis (CH$_3$CN): $\lambda_{\max}$ (lg ε) = 217 (sh, 4.362), 237 (4.243), 267 (4.569), 296 (4.062), 349 (3.751), 365 (3.951), 617 (2.577) nm. – MS (EI, 70 eV): *m/z* (%) = 701 (17) [M$^+$]. – HRMS: C$_{41}$H$_{53}$N$_2$O$_8$: calcd. 701.3802; found 701.3796.

2-[4-({6-[(4-{[4-(Dodecyloxy)benzoyl]oxy}-benzoyl)oxy]hexyl}oxy)phenyl]-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-3-imidazolio-1-oxyl (**14b**)

Compound **13d** (31 mg, 0.07 mmol) was esterified with **10** (25 mg, 0.07 mmol) according to the Steglich procedure [DMAP (5 mg), DCC (30 mg, 0.15 mmol), 24 h at r.t.]. The compound was purified by RC on silica gel with cyclohexane–ethyl acetate (3:2). Yield: 39 mg (72%), blue crystals, [7 mg (28%) of **13d** was recovered], m.p. 91.5 °C. – IR (KBr): ν = 2922, 2851, 1727, 1362, 1250, 1161 cm^{-1}. – UV/vis (CH$_3$CN): $\lambda_{\max}$ (lg ε) = 217 (3.768), 234 (3.881), 293 (3.951), 262 (3.604), 377 (3.828), 594 (2.036) nm. – MS (EI, 70 eV): *m/z* (%) = 757 (5) [M$^+$]. – HRMS: C$_{45}$H$_{61}$N$_2$O$_8$: calcd. 757.4428; found 757.4426.

---

[1] P. Kaszynski, in P. M. Lakti (ed.): Magnetic Properties of Organic Materials, pp. 305–324, Marcel Dekker, New York (1995).
[2] J. M. Farrar, M. K. Patel, P. Kaszynski, V. G. Young, J. Org. Chem. **65**, 931 (2000).
[3] J. H. Osiecki, E. F. Ullman, J. Am. Chem. Soc. **90**, 1078 (1968).
[4] Recent work: a) Y. Teki, S. Miyamoto, M. Nakatsuji, Y. Miura, J. Am. Chem. Soc. **123**, 294 (2001); b) A. Yamaguchi, K. Awaga, J. Mater. Chem. **11**, 2142 (2001); c) S. Hase, D. Shiomi, K. Sato, T. Takui, J. Mater. Chem. **11**, 756 (2001); d) S. Greve, C. Näther, W. Friedrichsen, Org. Lett. **2**, 2269 (2000); e) L. Catala, P. Turek, J. Le Moigne, A. De Cian, N. Kyritsakas, Tetrahedron Lett. **41**, 1015 (2000); f) O. Félix, M. W. Hosseini, A. De Cian, J. Fischer, L. Catala, P. Turek, Tetrahedron Lett. **40**, 2943 (1999); g) A. F. C. Alcântara, H. F. Dos Santos, W. B. De Almeida, M. G. F. Vaz, L. H. M. Pinheiro, H. O. Stumpf, Struct. Chem. **10**, 637 (1999); h) H. Heise, F. H. Köhler, F. Mota, J. J. Novoa, J. Veciana, J. Am. Chem. Soc. **121**, 9659 (1999); i) F. M. Romero, R. Ziessel, Tetrahedron Lett. **40**, 1895 (1999); j) C. Stroh, P. Turek, R. Ziessel, J. Chem. Soc., Chem. Commun. 2337 (1998); k) J. L. García-Muñoz, J. Cirujeda, J. Veciana, S. F. J. Cox, Chem. Phys. Lett. **293**, 160 (1998); l) K. Hamachi, K. Matsuda, H. Iwamura, Bull. Chem. Soc. Jpn. **71**, 2937 (1998). m) M. M. Matsushita, A. Izuoka, T. Sugawara, T. Kobayashi, N. Wada, N. Takeda, M. Ishikawa, J. Am. Chem. Soc. **119**, 4369 (1997) and references cited therein; n) Y. Kusaba, M. Tamura, Y. Hosokoshi, M. Kinoshita, H. Sawa, R. Kato, H. Kobayashi, J. Mater. Chem. **7**, 1377 (1997); o) C. Michaut, L. Ouahab, P. Bergerat, O. Kahn, A. Bousseksou, J. Am. Chem. Soc. **118**, 3610 (1996).
[5] a) J. S. Miller, Adv. Mater. **6**, 322 (1994); b) D. Gatteschi, Adv. Mater. **6**, 635 (1994); c) S. Nakatsuji, H. Anzai, J. Mater. Chem. **7**, 2161 (1997); d) W. Plass, Chem. Unserer Zeit **32**, 323 (1998).
[6] P. Turek, K. Nozawa, D. Shiomi, K. Awaga, T. Inabe, Y. Maruyama, M. Kinoshita, Chem. Phys. Lett. **180**, 327 (1991).
[7] See also : a) M. Kinoshita, Jpn. J. Appl. Phys. **33**, 5718 (1994); b) M. Deumal, J. Cirujeda, J. Veciana, J. J. Novoa, Adv. Mater. **10**, 1461 (1998).

[8] a) M. Buivydas, Phys. Status Solidi B **168**, 577 (1991); b) E. I. Kats, V. V. Lebedev, Mol. Cryst. Liq. Cryst. **209**, 329 (1991).

[9] Liquid crystalline aminoxides have been reported [10].

[10] a) M. Dvolaitzky, J. Billard, F. Poldy, C. R. Hebd. Seances Acad. Sci., Ser. C **279**, 533 (1974); b) M. Dvolaitzky, J. Billard, F. Poldy, Tetrahedron **32**, 1835 (1976).

[11] Handbook of Liquid Crystals (D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill, eds), Vol. 1, Wiley-VCH, Weinheim (1998).

[12] E. F. Ullman, J. H. Osiecki, D. G. B. Boocock, R. Darcy, J. Am. Chem. Soc. **94**, 7049 (1972).

[13] B. Neises, W. Steglich, Angew. Chem. **90**, 556 (1978); Angew. Chem., Int. Ed. Engl. **17**, 522 (1978).

[14] See, *e.g.*, J. March, Advanced Organic Chemistry, 3rd ed., Wiley, New York (1985).

[15] a) PHC7: R. Eidenschink, D. Erdmann, J. Krause, L. Pohl, Angew.Chem. **89**, 103 (1977); b) HOPDOB: D. Demus, H.-J. Deutscher, D. Marzotko, H. Kresse, A. Wiegeleben, in S. Chandrasehkar (ed.): Proc. Int. Conf. Liq. Cryst., p. 97, Bangalore (1980).

[16] a) PM3 calculations: T. Akita, K. Kobayashi, Tetrahedron **52**, 6893 (1996); b) CAS-SCF and DFT calculations for the parent system: S. Yamada, M. Nakano, K. Yamagushi, Int. J. Quant. Chem. **71**, 329 (1999); c) DFT calculations (UBLYP/6-31G* and UBLYP/6-31G): A. F. C. Alcântara, H. F. Dos Santos, W. B. De Almeida, M. G. F. Vaz, L. M. M. Pinheiro, H. O. Stumpf, Struct. Chem. **10**, 367 (1999); d) DFT calculations (BLYP/6-31G*): M. Minguet, D. B. Amabilino, J. Circujeda, K. Wurst, I. Mata, E. Molins, J. J. Novoa, J. Veciana, Chem. Eur. J. **6**, 2350 (2000).

[17] See, *e.g.*: a) J. J. P. Stewart, in K. B. Lipkowitz and D. B. Boyd (eds): Reviews in Computational Chemistry, p. 45, VCH Publ., New York (1990); b) M. C. Zerner, in K. B. Lipkowitz and D. B. Boyd (eds): Reviews in Computational Chemistry, Vol. 2, p. 313, VCH Publ., New York (1991); c) These calculations have been performed with the program system MOPAC 2000 for Windows, Fujitsu Ltd., Jpn.

[18] a) R. G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, Oxford (1989); b) J. K. Labanowsky, J. W. Andzelm, Density Functional Methods in Chemistry, Springer Verlag, New York (1991); c) T. Ziegler, Chem. Rev. **91**, 651 (1991); d) N. C. Handy, B. O. Roos (ed.): Lecture Notes in Chemistry II. European Summer School in Quantum Chemistry. Lecture Notes in Chemistry, Vol. 64, p. 91, Springer Verlag, New York (1994); e) A. D. Becke, J. Chem. Phys. **98**, 5468 (1993) and references cited therein; f) C. Lee, W. Yang, R. Parr, Phys. Rev. **41B**, 785 (1988); g) W. Koch, M. C. Holthusen, A Chemist's Guide to Density Functional Theory, 2nd ed., Wiley-VCH, Weinheim (2001).

[19] a) J. B. Foresman, Æ. Frisch, Exploring Chemistry with Electronic Structure Methods, 2nd ed., Gaussian, Inc., Pittsburgh, PA (1996); b) W. J. Hehre, L. Lou, A Guide to Density Functional calculations in SPARTAN, Wavefunction, Inc., Irvine, CA (1987).

[20] These calculations have been performed with the program systems Gaussian 98 [21], G98W [21] and Titan [22].

[21] Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, (Jr.), R. E Stratmann, J. C. Burant, S. Dapprich, J. M Millam, A. D Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA (1998).

[22] TITAN, Version 1, Schrödinger, Inc., Portland, OR (1999).

[23] M. Deumal, J. Cirujeda, J. Veciana, J. L. Novoa, Adv. Mater. **10**, 1461 (1998).

[24] For a similar modelling of liquid crystalline calixarenes (using Cerius) see: K. Yonetake, T. Nakayama, M. Ueda, J. Mater. Chem. **11**, 761 (2001).

[25] D. D. Perrin, W. L.-F. Armarego, Purification of Laboratory Chemicals, 3rd ed., Pergamon, Oxford (1989).

[26] S. M. Kelly, R. Buchecker, Helv. Chim. Acta **71**, 461 (1988).

[27] L. Gattermann, T. Wieland, Die Praxis des organischen Chemikers, 43. Aufl., p. 481, de Gruyter, Berlin, New York (1982).